REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

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1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)	
Dec 2014	Briefing Charts	Dec 2014- Dec 2014	
4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER		
		In-House	
Water Uptake Vs. Density and Convers	5b. GRANT NUMBER		
•			
	5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)	5d. PROJECT NUMBER		
6. AUTHOR(3)	Su. PROJECT NUMBER		
Michael D. Ford, Andrew J. Guent	5e. TASK NUMBER		
Michael D. Pold, Andrew J. Guent			
	5f. WORK UNIT NUMBER		
		Q0BG	
7. PERFORMING ORGANIZATION NAME(S	8. PERFORMING ORGANIZATION		
		REPORT NO.	
Air Force Research Laboratory (AFMC			
AFRL/RQRP			
10 E. Saturn Blvd.			
Edwards AFB CA 93524-7680			
9. SPONSORING / MONITORING AGENCY	NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)	
Air Force Research Laboratory (AFMC		(1,	
AFRL/RQR	,		
5 Pollux Drive		11. SPONSOR/MONITOR'S REPORT	
Edwards AFB CA 93524-7048		NUMBER(S)	
	AFRL-RQ-ED-VG-2014-330		
		AFRE-RQ-ED- 7 G-201 4- 330	

12. DISTRIBUTION / AVAILABILITY STATEMENT

Distribution A: Approved for Public Release; Distribution Unlimited.

13. SUPPLEMENTARY NOTES

Briefing Charts presented at Silicon-Containing Polymers and Composites, San Diego, CA, 15 December, 2014. PA#14581

14. ABSTRACT

A study was conducted which explored the density, percent water uptake by weight, and coefficient of thermal expansion as a function of conversion as measured by DSC in bis(4-cyanatophenyl)-dimethylsilane (SiMCy). The density of SiMCy was found to decrease with increasing conversion due to the formation of more free volume as the cyanurate networks cure, and this decline in density was found to be similar in magnitude to that of other cyanate ester resins which have been previously studied. The water uptake followed similar trends as compared to other cyanate esters in that it was similarly dependent on conversion, but did not correlate with the development of free volume except at high conversions (80%-100%). However, SiMCy did show a much lower percent water uptake as compared to other cyanate ester resins such as Bisphenol-E dicyanate (LECy). This data taken together would suggest that water has a much lower affinity for the cyanurate oxygens in SiMCy than in other cyanate esters.

15. SUBJECT TERMS

16. SECURITY CLAS	SIFICATION OF:		17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Joseph Mabry
a. REPORT	b. ABSTRACT	c. THIS PAGE	SAR	19	19b. TELEPHONE NO (include area code)
Unclassified	Unclassified	Unclassified	SAK		661-275-5857



Water Uptake Vs. Density and Conversion in Silicon Containing Cyanate Esters

17 December 2014

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Outline



- Background
- Density as a Function of Conversion
 - Uncatalyzed and catalyzed LECy
 - Uncatalyzed and catalyzed SiMCy
 - Catalyzed BADCy
- Water Uptake as a Function of Conversion
 - Uncatalyzed SiMCy and LECy









Background



- New methods of density measurement allow for 3x improvement in precision of density determination (typical error ~0.001 g/cc) with greatly reduced effort
- New methods of conversion measurement allow for a simialr 3x improvement in precision (typical error now 0.01 – 0.02 or better across a broad range of conversion)
- Improved methods allow for quantitative investigation of issues that previously could only be addressed through qualitative studies
- Qualitatively, it is known that cyanate ester networks decrease in density as conversion increases, and that moisture uptake increases as conversion increases at conversions greater than 0.8
- It is speculated that the lower densities allow for greater free volume, which can accommodate more water in micro-voids within the network
- Quantitative studies can help to confirm or refute this model, as well as test applicability to different types of cyanate ester networks (flexible vs. rigid backbones), along with differences between catalyzed and uncatalyzed networks.



Materials and Methods



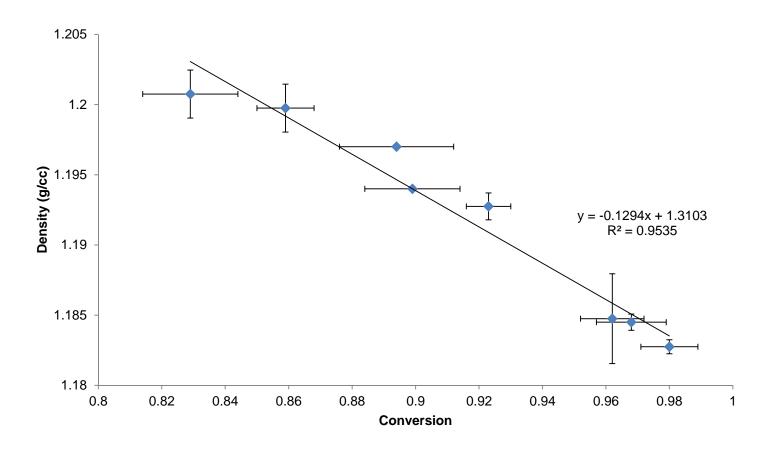
Name	MW (g/mol)
BADCy	278.3
LECy	264.3
SiMCy	294.4

- "SiMCy"
- LECy is slightly smaller and more flexible than BADCy due to the missing methyl group
 - SiMCy is slightly larger than BADCy due to the longer Si-C bonds, but also more flexible
- Density determination method: measure specific gravity by immersion in ethanol and air (Mettler-Toledo balance with specific gravity kit added).
- Conversions and Tg values were measured by DSC using a heating rate of 10
 °C / min, with two scans to 350 °C for "as cured" and "fully cured" values,
 respectively.



Catalyzed BADCy Data



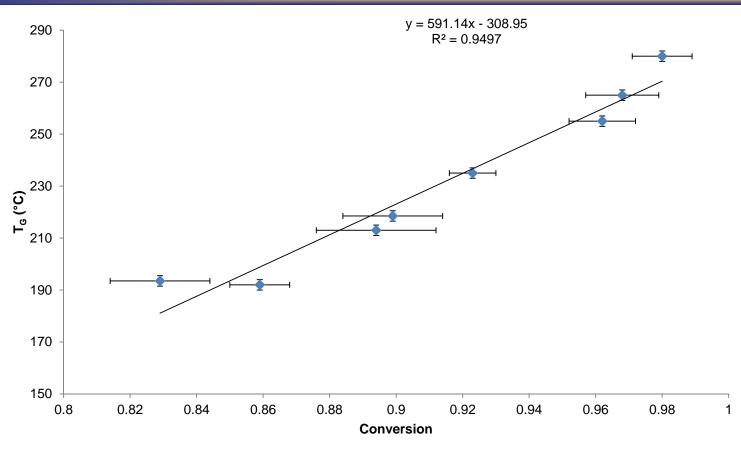


Catalyzed BADCy, Density vs. Conversion



Catalyzed BADCy Data

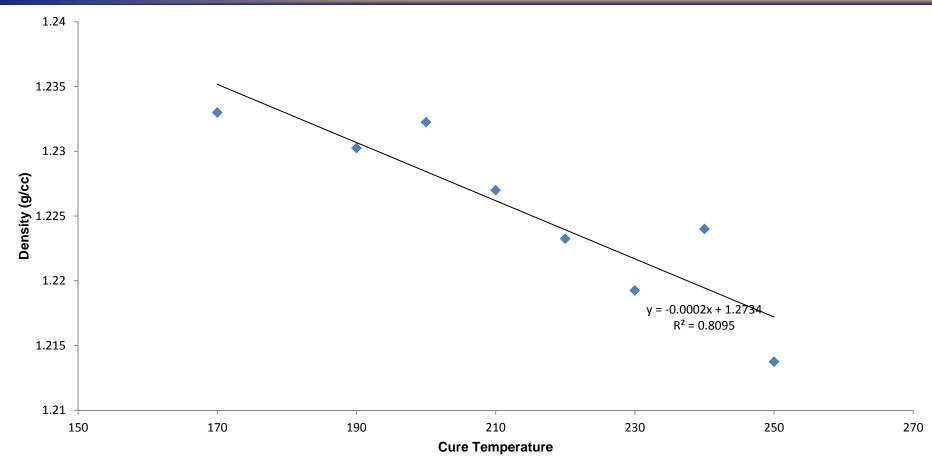




Catalyzed BADCy, Tg vs. Conversion; follows diBenedetto equation



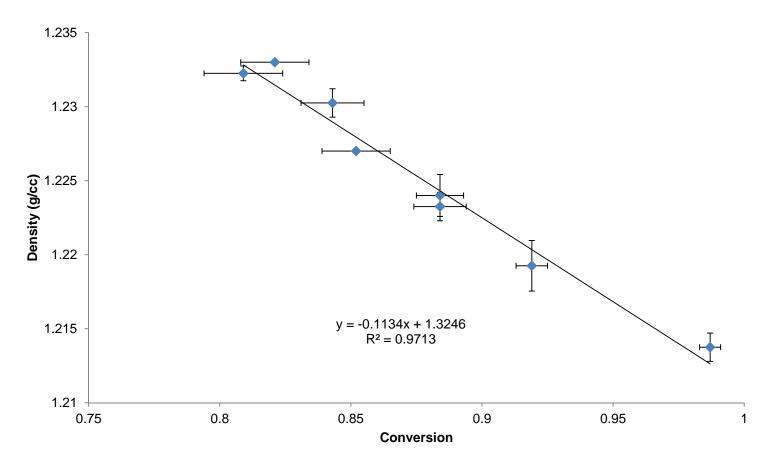




Uncatalyzed LECy, Density vs. Cure Temperature



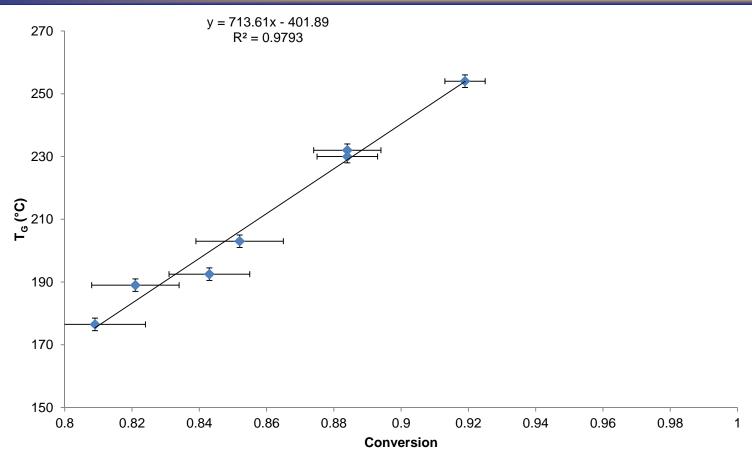




Uncatalyzed LECy, Density vs. Conversion



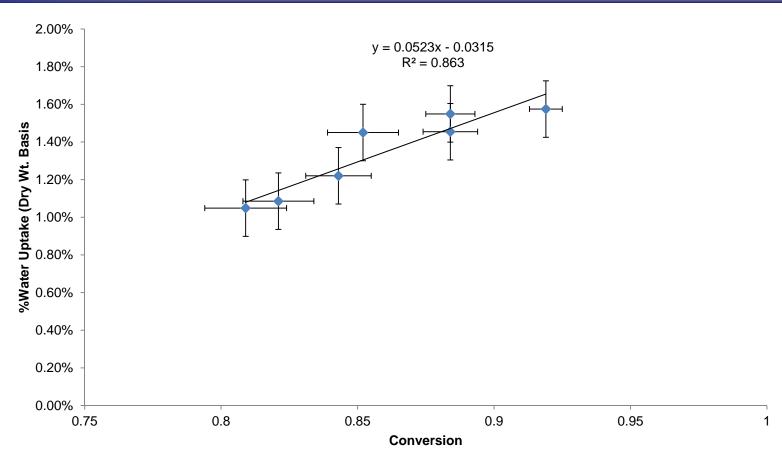




Uncatalyzed LECy, Tg vs. Conversion; follows diBenedetto equation





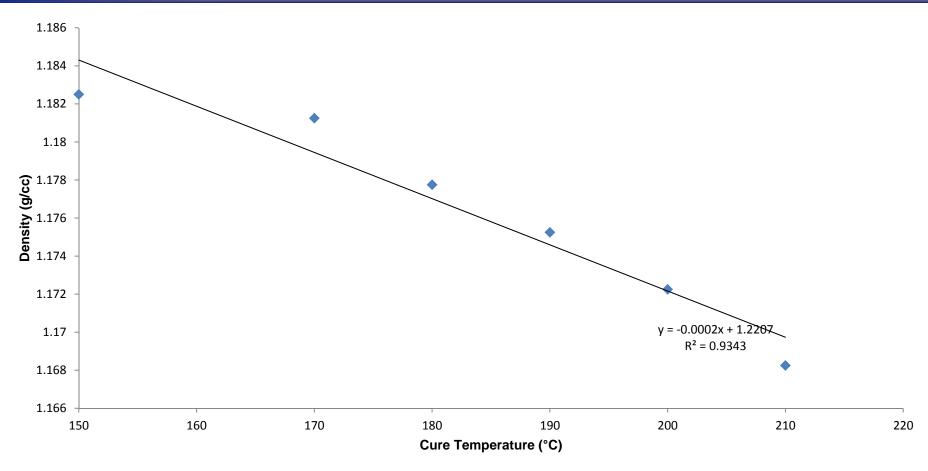


Uncatalyzed LECy, %Water Uptake vs. Conversion



Catalyzed SiMCy Data



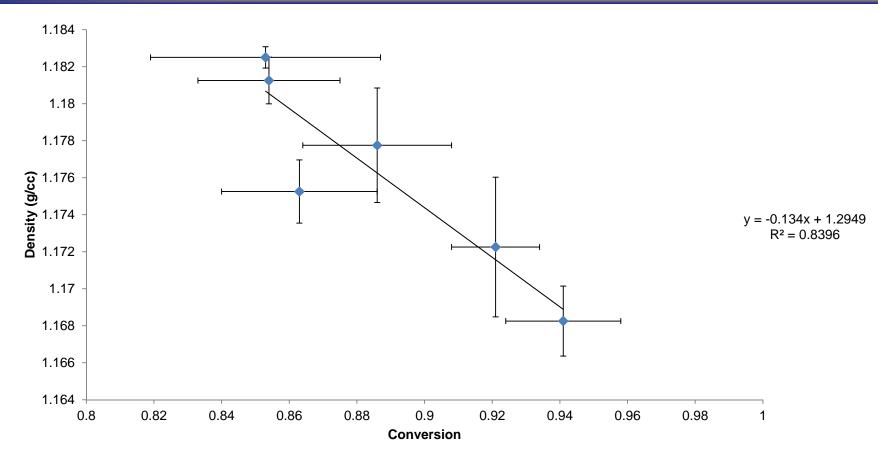


Catalyzed SiMCy, Density vs. Cure Temperature



Catalyzed SiMCy Data



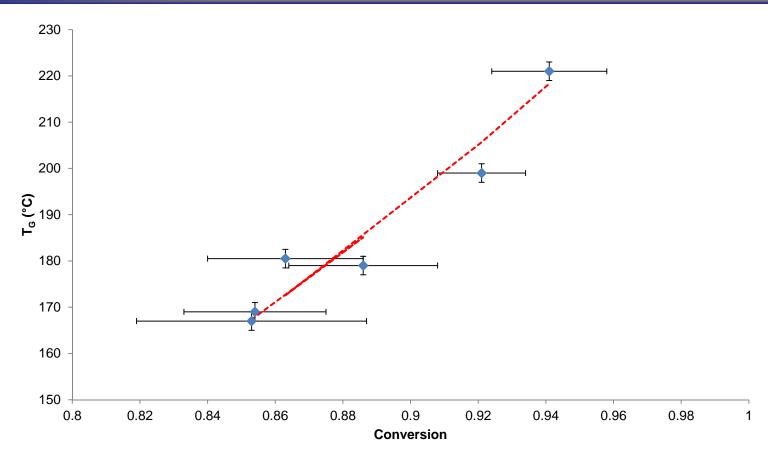


Catalyzed SiMCy, Density vs. Conversion



Catalyzed SiMCy Data



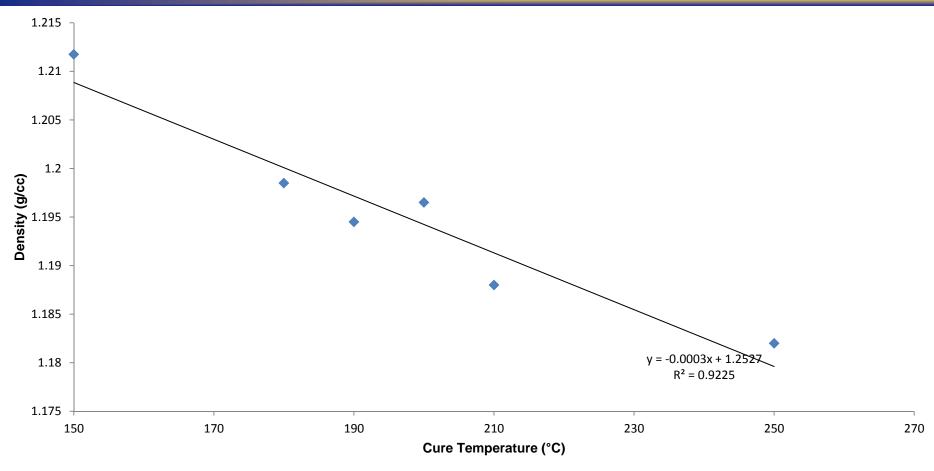


 Catalyzed SiMCy, Tg vs. Conversion, with fitted diBenedetto equation shown



Uncatalyzed SiMCy Data



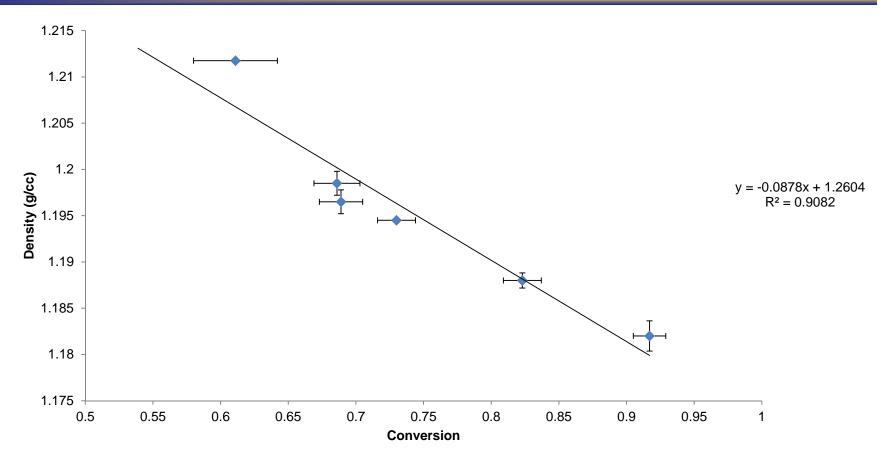


Uncatalyzed SiMCy, Density vs. Cure Temperature



Uncatalyzed SiMCy Data



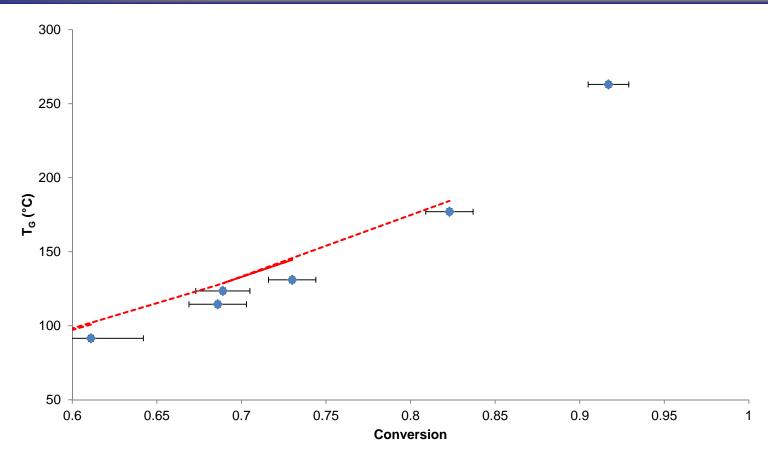


Uncatalyzed SiMCy, Density vs. Conversion



Uncatalyzed SiMCy Data





 Uncatalyzed SiMCy, Tg vs. Conversion, with DiBenedetto Equation Fit Shown



Summary



- As expected, higher cure temperatures lead to higher conversions due to vitrification effects
- Density vs. conversion data show a remarkably linear dependence across a broad range of conversions. At a given conversion, the trend BADCy > LECy > SiMCy, and the negative effect of catalyst inclusion on density, are all confirmed.
- Tg vs. conversion data follow the diBenedetto equation as expected, with the plasticizing effect of catalyst inclusion clearly distinguishable.
- Water uptake vs. conversion shows clear non-linear behavior and is not directly related to density. Water uptake may be influenced by both the loss in density and the formation of hydrophilic side products at higher cure temperatures.
- The water uptake for SiMCy is lower than for BADCy at all conversions studied, despite higher free volume in SiMCy, and similar increases in free volume with conversion. SiMCy appears to have an intrinsically lower affinity for water uptake.

